

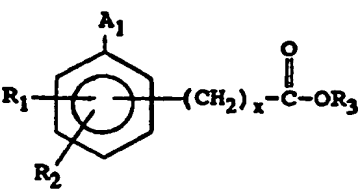
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(21) International Application Number: PCT/US94/13797 (22) International Filing Date: 2 December 1994 (02.12.94) (30) Priority Data: 08/162,416 3 December 1993 (03.12.93) US (71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).	(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: POLYALKYL NITRO AND AMINO AROMATIC ESTERS AND FUEL COMPOSITIONS CONTAINING THE SAME (57) Abstract <p>Polyalkyl nitro and amino aromatic esters having formula (I): wherein A₁ is nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms; R₁ and R₂ are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10. The polyalkyl nitro and amino aromatic esters of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p> <div style="text-align: center;">  <p style="text-align: right;">(I)</p> </div>		

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-1-

POLYALKYL NITRO AND AMINO AROMATIC ESTERS
AND FUEL COMPOSITIONS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel nitro and amino aromatic compounds. More particularly, this invention relates to novel polyalkyl nitro and amino aromatic esters and their use in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the

-2-

01 gasoline boiling range containing about 0.01 to 0.25 volume
02 percent of a high molecular weight aliphatic
03 hydrocarbon-substituted phenol in which the aliphatic
04 hydrocarbon radical has an average molecular weight in the
05 range of about 500 to 3,500. This patent teaches that
06 gasoline compositions containing minor amounts of an
07 aliphatic hydrocarbon-substituted phenol not only prevent or
08 inhibit the formation of intake valve and port deposits in a
09 gasoline engine, but also enhance the performance of the
10 fuel composition in engines designed to operate at higher
11 operating temperatures with a minimum of decomposition and
12 deposit formation in the manifold of the engine.
13

14 Similarly, U.S. Patent No. 4,134,846, issued January 16,
15 1979 to Machleder et al., discloses a fuel additive
16 composition comprising a mixture of (1) the reaction product
17 of an aliphatic hydrocarbon-substituted phenol,
18 epichlorohydrin and a primary or secondary mono- or
19 polyamine, and (2) a polyalkylene phenol. This patent
20 teaches that such compositions show excellent carburetor,
21 induction system and combustion chamber detergency and, in
22 addition, provide effective rust inhibition when used in
23 hydrocarbon fuels at low concentrations.
24

25 Amino phenols are also known to function as
26 detergents/dispersants, antioxidants and anti-corrosion
27 agents when used in fuel compositions. U.S. Patent
28 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
29 example, discloses amino phenols having at least one
30 substantially saturated hydrocarbon-based substituent of at
31 least 30 carbon atoms. The amino phenols of this patent are
32 taught to impart useful and desirable properties to
33 oil-based lubricants and normally liquid fuels. Similar
34

-3-

01 amino phenols are disclosed in related U.S. Patent
02 No. 4,320,020, issued March 16, 1982 to R. M. Lange.
03

04 Similarly, U.S. Patent No. 3,149,933, issued September 22,
05 1964 to K. Ley et al., discloses hydrocarbon-substituted
06 amino phenols as stabilizers for liquid fuels.
07

08 U.S. Patent No. 4,386,939, issued June 7, 1983 to
09 R. M. Lange, discloses nitrogen-containing compositions
10 prepared by reacting an amino phenol with at least one 3- or
11 4-membered ring heterocyclic compound in which the hetero
12 atom is a single oxygen, sulfur or nitrogen atom, such as
13 ethylene oxide. The nitrogen-containing compositions of
14 this patent are taught to be useful as additives for
15 lubricants and fuels.
16

17 Nitro phenols have also been employed as fuel additives.
18 For example, U.S. Patent No. 4,347,148, issued August 31,
19 1982 to K. E. Davis, discloses nitro phenols containing at
20 least one aliphatic substituent having at least about 40
21 carbon atoms. The nitro phenols of this patent are taught
22 to be useful as detergents, dispersants, antioxidants and
23 demulsifiers for lubricating oil and fuel compositions.
24

25 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969
26 to M. Dubeck et al., discloses a liquid hydrocarbon fuel
27 composition containing a major quantity of a liquid
28 hydrocarbon of the gasoline boiling range and a minor amount
29 sufficient to reduce exhaust emissions and engine deposits
30 of an aromatic nitro compound having an alkyl, aryl,
31 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen
32 substituent.
33
34

-4-

01 More recently, certain poly(oxyalkylene) esters have been
02 shown to reduce engine deposits when used in fuel
03 compositions. U.S. Patent No. 5,211,721, issued May 18,
04 1993 to R. L. Sung et al., for example, discloses an oil
05 soluble polyether additive comprising the reaction product
06 of a polyether polyol with an acid represented by the
07 formula RCOOH in which R is a hydrocarbyl radical having
08 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds
09 of this patent are taught to be useful for inhibiting
10 carbonaceous deposit formation, motor fuel hazing, and as
11 ORI inhibitors when employed as soluble additives in motor
12 fuel compositions.

13
14 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids
15 are also known in the art. For example, U.S. Patent
16 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses
17 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids
18 and other isocyclic acids. These polyethoxy esters are
19 taught to have excellent pharmacological properties and to
20 be useful as anesthetics, spasmolytics, analeptics and
21 bacteriostatics.

22
23 Similarly, U.S. Patent No. 5,090,914, issued February 25,
24 1992 to D. T. Reardan et al., discloses poly(oxyalkylene)
25 aromatic compounds having an amino or hydrazinocarbonyl
26 substituent on the aromatic moiety and an ester, amide,
27 carbamate, urea or ether linking group between the aromatic
28 moiety and the poly(oxyalkylene) moiety. These compounds
29 are taught to be useful for modifying macromolecular species
30 such as proteins and enzymes.

31
32 U.S. Patent No. 4,328,322, issued September 22, 1980 to
33 R. C. Baron, discloses amino- and nitrobenzoate esters of
34 oligomeric polyols, such as poly(ethylene) glycol. These

01 materials are used in the production of synthetic polymers
02 by reaction with a polyisocyanate.

03

04 In addition, U.S. Patent No. 4,231,759, issued November 4,
05 1980 to Udelhofen et al., discloses a fuel additive
06 composition comprising the Mannich condensation product of
07 (1) a high molecular weight alkyl-substituted
08 hydroxyaromatic compound wherein the alkyl group has a
09 number average molecular weight of about 600 to about 3,000,
10 (2) an amine, and (3) an aldehyde. This patent teaches that
11 such Mannich condensation products provide carburetor
12 cleanliness when employed alone, and intake valve
13 cleanliness when employed in combination with a hydrocarbon
14 carrier fluid.

15

16 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz
17 et al., discloses fuel compositions containing (1) one or
18 more polybutyl or polyisobutyl alcohols wherein the
19 polybutyl or polyisobutyl group has a number average
20 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
21 of the polybutyl or polyisobutyl alcohol, or (3) a
22 carboxylate ester of the polybutyl or polyisobutyl alcohol.
23 This patent further teaches that when the fuel composition
24 contains an ester of a polybutyl or polyisobutyl alcohol,
25 the ester-forming acid group may be derived from saturated
26 or unsaturated, aliphatic or aromatic, acyclic or cyclic
27 mono- or polycarboxylic acids.

28

29 U.S. Patent No. 3,285,855, issued November 15, 1966 to
30 Dexter et al., discloses alkyl esters of dialkyl
31 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the
32 ester moiety contains from 6 to 30 carbon atoms. This
33 patent teaches that such esters are useful for stabilizing
34 polypropylene and other organic material normally subject to

-6-

01 oxidative deterioration. Similar alkyl esters containing
02 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.
03 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

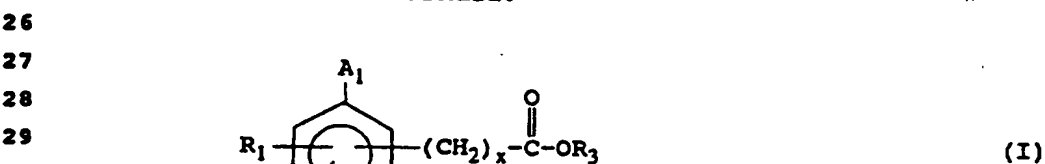
04
05 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet
06 et al., discloses alkyl esters of hydroxyphenyl carboxylic
07 acids wherein the ester moiety may contain up to 23 carbon
08 atoms. This patent teaches that such compounds are useful
09 as antioxidants for stabilizing emulsion-polymerized
10 polymers.

11
12 It has now been discovered that certain polyalkyl nitro and
13 amino aromatic esters provide excellent control of engine
14 deposits, especially intake valve deposits, when employed as
15 fuel additives in fuel compositions.

16
17 SUMMARY OF THE INVENTION

18
19 The present invention provides novel polyalkyl nitro and
20 amino aromatic esters which are useful as fuel additives for
21 the prevention and control of engine deposits, particularly
22 intake valve deposits.

23
24 The polyalkyl nitro and amino aromatic esters of the present
25 invention have the formula:



-7-

01 wherein A_1 is nitro, amino, *N*-alkylamino wherein the alkyl
02 group contains 1 to 6 carbon atoms, or *N,N*-dialkylamino
03 wherein each alkyl group independently contains 1 to 6
04 carbon atoms; R_1 and R_2 are each independently hydrogen,
05 hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower
06 alkoxy having 1 to 6 carbon atoms; R_3 is a polyalkyl group
07 having a weight average molecular weight in the range of
08 about 450 to 5,000; and x is an integer from 0 to 10.
09

10 The present invention further provides a fuel composition
11 comprising a major amount of hydrocarbons boiling in the
12 gasoline or diesel range and an effective
13 deposit-controlling amount of a polyalkyl nitro or amino
14 aromatic ester of the present invention.
15

16 The present invention additionally provides a fuel
17 concentrate comprising an inert stable oleophilic organic
18 solvent boiling in the range of from about 150°F to 400°F
19 and from about 10 to 70 weight percent of a polyalkyl nitro
20 or amino aromatic ester of the present invention.
21

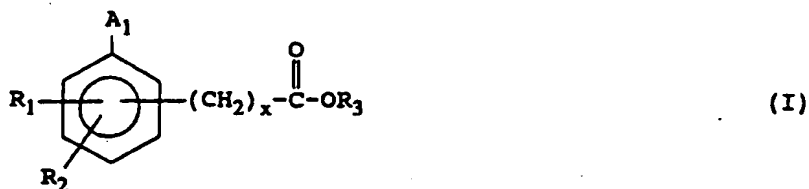
22 Among other factors, the present invention is based on the
23 surprising discovery that certain polyalkyl nitro and amino
24 aromatic esters provide excellent control of engine
25 deposits, especially on intake valves, when employed as fuel
26 additives in fuel compositions.
27

28 DETAILED DESCRIPTION OF THE INVENTION

29

30 The fuel additives provided by the present invention have
31 the general formula:
32
33
34

-8-



14 wherein A_1 , R_1 , R_2 , R_3 , and x are as defined hereinabove.

15 In formula I, A_1 is preferably a nitro, amino, or
16 *N*-alkylamino group. More preferably, A_1 is a nitro or amino
17 group. Most preferably, A_1 is an amino group.

18 Preferably, R_1 is hydrogen, hydroxy, or lower alkyl having 1
19 to 4 carbon atoms. More preferably, R_1 is hydrogen or
20 hydroxy. Most preferably, R_1 is hydroxy.

21 R_2 is preferably hydrogen.

22 Preferably, R_3 is a polyalkyl group having a weight average
23 molecular weight in the range of about 500 to 5,000, more
24 preferably about 500 to 3,000, and most preferably about 600
25 to 2,000.

26 Preferably, x is an integer from 0 to 2. More preferably,
27 x is 0.

28 A preferred group of polyalkyl aromatic esters are those of
29 formula I wherein R_1 is hydrogen, hydroxy, or lower alkyl
30 having 1 to 4 carbon atoms; R_2 is hydrogen; and x is 0.

31 Another preferred group of polyalkyl aromatic esters are
32 those of formula I wherein R_1 is hydrogen, hydroxy, or lower
33 alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; and x is 0.
34

01 alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; and x is 1
02 or 2.

03

04 A more preferred group of polyalkyl aromatic esters are
05 those of formula I wherein R_1 is hydrogen or hydroxy; R_2 is
06 hydrogen; and x is 0.

07

08 A particularly preferred group of polyalkyl aromatic esters
09 are those wherein R_1 is hydroxy, R_2 is hydrogen, and x is 0.

10

11 When A_1 is an *N*-alkylamino group, the alkyl group of the
12 *N*-alkylamino moiety preferably contains 1 to 4 carbon atoms.
13 More preferably, the alkyl group is methyl or ethyl. For
14 example, particularly preferred *N*-alkylamino groups are
15 *N*-methylamino and *N*-ethylamino groups.

16

17 Similarly, when A_1 is an *N,N*-dialkylamino group, each alkyl
18 group of the *N,N*-dialkylamino moiety preferably contains 1
19 to 4 carbon atoms. More preferably, each alkyl group is
20 either methyl or ethyl. For example, particularly preferred
21 *N,N*-dialkylamino groups are *N,N*-dimethylamino,
22 *N*-ethyl-*N*-methylamino and *N,N*-diethylamino groups.

23

24 A further preferred group of polyalkyl aromatic esters are
25 those wherein A_1 is amino or nitro, R_1 is hydrogen or
26 hydroxy, R_2 is hydrogen, and x is 0, 1 or 2. A more
27 preferred group of polyalkyl aromatic esters are those
28 wherein A_1 is amino or nitro, R_1 is hydrogen or hydroxy, R_2
29 is hydrogen, and x is 0. A particularly preferred group of
30 polyalkyl aromatic esters are those wherein A_1 is amino or
31 nitro, R_1 is hydroxy, R_2 is hydrogen, and x is 0.

32

33

34

-10-

01 It is especially preferred that the nitro, amino,
02 *N*-alkylamino or *N,N*-dialkylamino substituent present in the
03 aromatic moiety of the polyalkyl aromatic esters of this
04 invention be situated in a *meta* or *para* position relative to
05 the polyalkyl ester moiety. When the aromatic moiety also
06 contains a hydroxyl substituent, it is particularly
07 preferred that this hydroxyl group be in a *meta* or *para*
08 position relative to the polyalkyl ester moiety and in an
09 *ortho* position relative to the nitro, amino, *N*-alkylamino or
10 *N,N*-dialkylamino substituent.

11
12 The polyalkyl aromatic esters of the present invention will
13 generally have a sufficient molecular weight so as to be
14 non-volatile at normal engine intake valve operating
15 temperatures (about 200-250°C). Typically, the molecular
16 weight of the polyalkyl hydroxyaromatic esters of this
17 invention will range from about 600 to about 6,000,
18 preferably from 600 to 3,000, more preferably from 700 to
19 2,000.

20
21 Fuel-soluble salts of the polyalkyl aromatic esters of the
22 present invention can be readily prepared for those
23 compounds containing an amino, *N*-alkylamino or
24 *N,N*-dialkylamino group and such salts are contemplated to be
25 useful for preventing or controlling engine deposits.
26 Suitable salts include, for example, those obtained by
27 protonating the amino moiety with a strong organic acid,
28 such as an alkyl- or arylsulfonic acid. Preferred salts are
29 derived from toluenesulfonic acid and methanesulfonic acid.

30
31 Definitions
32

33 As used herein, the following terms have the following
34 meanings unless expressly stated to the contrary.

-11-

01 The term "amino" refers to the group: -NH_2 .

02

03 The term "N-alkylamino" refers to the group: -NHR_1 wherein
04 R_1 is an alkyl group. The term "N,N-dialkylamino" refers to
05 the group: $\text{-NR}_b\text{R}_c$, wherein R_b and R_c are alkyl groups.

06

07 The term "alkyl" refers to both straight- and branched-chain
08 alkyl groups.

09

10 The term "lower alkyl" refers to alkyl groups having 1 to
11 about 6 carbon atoms and includes primary, secondary and
12 tertiary alkyl groups. Typical lower alkyl groups include,
13 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
14 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

15

16 The term "lower alkoxy" refers to the group -OR_d wherein R_d
17 is lower alkyl. Typical lower alkoxy groups include
18 methoxy, ethoxy, and the like.

19

20 The term "polyalkyl" refers to alkyl groups which are
21 generally derived from polyolefins which are polymers or
22 copolymers of mono-olefins, particularly 1-mono-olefins,
23 such as ethylene, propylene, butylene, and the like.
24 Preferably, the mono-olefin employed will have 2 to about
25 24 carbon atoms, and more preferably, about 3 to 12 carbon
26 atoms. More preferred mono-olefins include propylene,
27 butylene, particularly isobutylene, 1-octene and 1-decene.
28 Polyolefins prepared from such mono-olefins include
29 polypropylene, polybutene, especially polyisobutene, and the
30 polyalphaolefins produced from 1-octene and 1-decene.

31

32

33

34

-12-

01 General Synthetic Procedures

02

03 The polyalkyl nitro and amino aromatic esters of this
04 invention may be prepared by the following general methods
05 and procedures. It should be appreciated that where typical
06 or preferred process conditions (e.g., reaction
07 temperatures, times, mole ratios of reactants, solvents,
08 pressures, etc.) are given, other process conditions may
09 also be used unless otherwise stated. Optimum reaction
10 conditions may vary with the particular reactants or
11 solvents used, but such conditions can be determined by one
12 skilled in the art by routine optimization procedures.

13

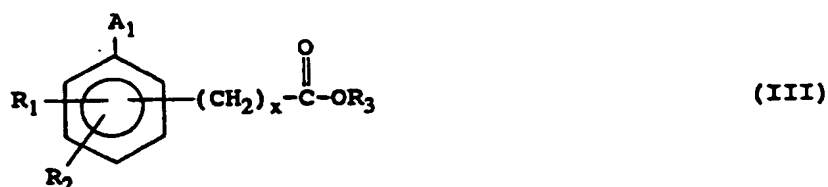
14 Moreover, those skilled in the art will recognize that it
15 may be necessary to block or protect certain functional
16 groups while conducting the following synthetic procedures.
17 In such cases, the protecting group will serve to protect
18 the functional group from undesired reactions or to block
19 its undesired reaction with other functional groups or with
20 the reagents used to carry out the desired chemical
21 transformations. The proper choice of a protecting group
22 for a particular functional group will be readily apparent
23 to one skilled in the art. Various protecting groups and
24 their introduction and removal are described, for example,
25 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
26 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
27 and references cited therein.

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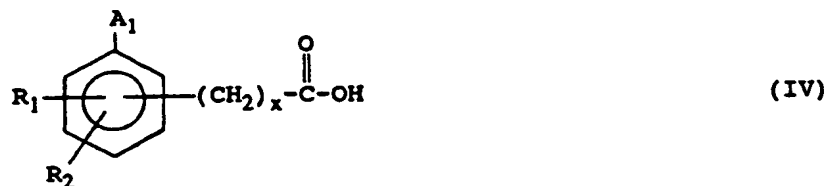
29 In the present synthetic procedures, a hydroxyl group will
30 preferably be protected, when necessary, as the benzyl or
31 *tert*-butyldimethylsilyl ether. Introduction and removal of
32 these protecting groups is well described in the art. Amino
33 groups may also require protection and this may be
34 accomplished by employing a standard amino protecting group,

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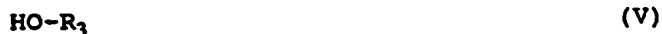
01 such as a benzyloxycarbonyl or a trifluoroacetyl group.
02 Additionally, as will be discussed in further detail
03 hereinbelow, the polyalkyl aromatic esters of this invention
04 having an amino group on the aromatic moiety will generally
05 be prepared from the corresponding nitro derivative.
06 Accordingly, in many of the following procedures, a nitro
07 group will serve as a protecting group for the amino moiety.
08
09 The polyalkyl aromatic esters of the present invention
10 having the formula:



23 wherein A_1 , R_1 , R_2 , R_3 and x are as defined above, may be
24 prepared by esterifying an aromatic carboxylic acid having
25 the formula:



35 wherein A_1 , R_1 , R_2 , and x are as defined above, with a
36 polyalkyl alcohol having the formula:



-14-

01 wherein R₃ is as defined above, using conventional
02 esterification reaction conditions.

03

04 The aromatic carboxylic acids of formula IV are either known
05 compounds or can be prepared from known compounds by
06 conventional procedures. Representative aromatic carboxylic
07 acids suitable for use as starting materials include, for
08 example, 2-aminobenzoic acid (anthranilic acid),
09 3-aminobenzoic acid, 4-aminobenzoic acid,
10 3-amino-4-hydroxybenzoic acid, 4-amino-3-hydroxybenzoic
11 acid, 3-aminophenylacetic acid, 4-aminophenylacetic acid,
12 3-amino-4-methoxybenzoic acid, 4-amino-3-methoxybenzoic
13 acid, 4-amino-3-methylbenzoic acid,
14 4-amino-3,5-di-*t*-butylbenzoic acid, 2-nitrobenzoic acid,
15 3-nitrobenzoic acid, 4-nitrobenzoic acid,
16 2-nitrophenylacetic acid, 3-nitrophenylacetic acid,
17 4-nitrophenylacetic acid, 3-hydroxy-4-nitrobenzoic acid,
18 4-hydroxy-3-nitrobenzoic acid, 4-hydroxy-3-nitrophenylacetic
19 acid, 3-(*N*-methylamino)benzoic acid,
20 4-(*N*-methylamino)benzoic acid, 3-(*N*-ethylamino)benzoic acid,
21 4-(*N*-ethylamino)benzoic acid, 3-(*N,N*-dimethylamino)benzoic
22 acid, 4-(*N,N*-dimethylamino)benzoic acid, and the like.

23

24 Preferred aromatic carboxylic acids include 3-aminobenzoic
25 acid, 4-aminobenzoic acid, 3-amino-4-hydroxybenzoic acid,
26 4-amino-3-hydroxybenzoic acid, 3-nitrobenzoic acid,
27 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic and
28 4-hydroxy-3-nitrobenzoic acid.

29

30 The polyalkyl alcohols of formula V may also be prepared by
31 conventional procedures known in the art. Such procedures
32 are taught, for example, in U.S. Patent Nos. 5,055,607 to
33

34

-15-

01 Buckley and 4,859,210 to Franz et al., the disclosures of
02 which are incorporated herein by reference.
03

04 In general, the polyalkyl substituent on the polyalkyl
05 alcohols of Formula V and the resulting polyalkyl aromatic
06 esters of the present invention will have a weight average
07 molecular weight in the range of about 450 to 5,000,
08 preferably about 500 to 5,000, more preferably about 500 to
09 3,000, and most preferably about 600 to 2,000.
10

11 The polyalkyl substituent on the polyalkyl alcohols employed
12 in the invention may be generally derived from polyolefins
13 which are polymers or copolymers of mono-olefins,
14 particularly 1-mono-olefins, such as ethylene, propylene,
15 butylene, and the like. Preferably, the mono-olefin
16 employed will have 2 to about 24 carbon atoms, and more
17 preferably, about 3 to 12 carbon atoms. More preferred
18 mono-olefins include propylene, butylene, particularly
19 isobutylene, 1-octene and 1-decene. Polyolefins prepared
20 from such mono-olefins include polypropylene, polybutene,
21 especially polyisobutene, and the polyalphaolefins produced
22 from 1-octene and 1-decene.
23

24 The preferred polyisobutenes used to prepare the presently
25 employed polyalkyl alcohols are polyisobutenes which
26 comprise at least about 20% of the more reactive
27 methylvinylidene isomer, preferably at least 50% and more
28 preferably at least 70%. Suitable polyisobutenes include
29 those prepared using BF_3 catalysts. The preparation of such
30 polyisobutenes in which the methylvinylidene isomer
31 comprises a high percentage of the total composition is
32 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such
33 polyisobutenes, known as "reactive" polyisobutenes, yield
34

-16-

01 high molecular weight alcohols in which the hydroxyl group
02 is at or near the end of the hydrocarbon chain.

03

04 Examples of suitable polyisobutenes having a high
05 alkylvinylidene content include Ultravis 30, a polyisobutene
06 having a molecular weight of about 1300 and a
07 methylvinylidene content of about 74%, and Ultravis 10, a
08 polyisobutene having a molecular weight of about 950 and a
09 methylvinylidene content of about 76%, both available from
10 British Petroleum.

11

12 The polyalkyl alcohols may be prepared from the
13 corresponding olefins by conventional procedures. Such
14 procedures include hydration of the double bond to give an
15 alcohol. Suitable procedures for preparing such long-chain
16 alcohols are described in I. T. Harrison and S. Harrison,
17 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,
18 New York (1971), pp. 119-122, as well as in U.S. Patent
19 Nos. 5,055,607 and 4,859,210.

20

21 As indicated above, the polyalkyl aromatic esters of formula
22 III may be prepared by esterifying an aromatic carboxylic
23 acid of formula IV with a polyalkyl alcohol of formula V
24 under conventional esterification reaction conditions.

25

26 Typically, this reaction will be conducted by contacting a
27 polyalkyl alcohol of formula V with about 0.25 to about 1.5
28 molar equivalents of an aromatic carboxylic acid of formula
29 IV in the presence of an acidic catalyst at a temperature in
30 the range of about 70°C to about 160°C for about 0.5 to
31 about 48 hours. Suitable acid catalysts for this reaction
32 include p-toluene sulfonic acid, methanesulfonic acid and
33 the like. The reaction may be conducted in the presence or
34 absence of an inert solvent, such as benzene, toluene and

-17-

01 the like. The water generated by this reaction is
02 preferably removed during the course of the reaction by, for
03 example, azeotropic distillation with an inert solvent, such
04 as toluene.

05

06 Alternatively, the polyalkyl aromatic esters of formula III
07 may be prepared by reacting a polyalkyl alcohol of formula V
08 with an acid halide derived from an aromatic carboxylic acid
09 of formula IV, such as an acid chloride or acid bromide.

10

11 Generally, the carboxylic acid moiety of formula IV may be
12 converted into an acyl halide moiety by contacting a
13 compound of formula IV with an inorganic acid halide, such
14 as thionyl chloride, phosphorous trichloride, phosphorous
15 tribromide, or phosphorous pentachloride; or with oxalyl
16 chloride. Typically, this reaction will be conducted using
17 about 1 to 5 molar equivalents of the inorganic acid halide
18 or oxalyl chloride, either neat or in an inert solvent, such
19 as diethyl ether, at a temperature in the range of about
20 20°C to about 80°C for about 1 to about 48 hours. A
21 catalyst, such as *N,N*-dimethylformamide, may also be used in
22 this reaction.

23

24 Reaction of the acid halide derived from formula IV with a
25 polyalkyl alcohol of formula V provides a polyalkyl aromatic
26 ester of formula III. Typically, this reaction is conducted
27 by contacting formula V with about 0.9 to about 1.5 molar
28 equivalents of the acid halide in an inert solvent, such as
29 toluene, dichloromethane, diethyl ether, and the like, at a
30 temperature in the range of about 25°C to about 150°C. The
31 reaction is generally complete in about 0.5 to about
32 48 hours. Preferably, the reaction is conducted in the
33 presence of a sufficient amount of an amine capable of
34 neutralizing the acid generated during the reaction, such as

-18-

01 triethylamine, di(isopropyl)ethylamine, pyridine or
02 4-dimethylaminopyridine.

03

04 When the aromatic carboxylic acid of formula IV contains a
05 hydroxyl group, for example, when R₁ or R₂ is hydroxyl,
06 protection of the aromatic hydroxyl groups may be
07 accomplished using well-known procedures. The choice of a
08 suitable protecting group for a particular hydroxyaromatic
09 carboxylic acid will be apparent to those skilled in the
10 art. Various protecting groups, and their introduction and
11 removal, are described, for example, in T. W. Greene and
12 P. G. M. Wuts, *Protective Groups in Organic Synthesis*,
13 Second Edition, Wiley, New York, 1991, and references cited
14 therein.

15

16 Deprotection of the aromatic hydroxyl group(s) can also be
17 accomplished using conventional procedures. Appropriate
18 conditions for this deprotection step will depend upon the
19 protecting group(s) utilized in the synthesis and will be
20 readily apparent to those skilled in the art. For example,
21 benzyl protecting groups may be removed by hydrogenolysis
22 under 1 to about 4 atmospheres of hydrogen in the presence
23 of a catalyst, such as palladium on carbon. Typically, this
24 deprotection reaction is conducted in an inert solvent,
25 preferably a mixture of ethyl acetate and acetic acid, at a
26 temperature of from about 0°C to about 40°C for about 1 to
27 about 24 hours.

28

29 When synthesizing the polyalkyl aromatic esters of formula I
30 having an amino group on the aromatic moiety (i.e., where A₁
31 is an amino group), it is generally desirable to first
32 prepare the corresponding nitro compound (i.e., where A₁ is
33 a nitro group) using the above-described synthetic
34

-19-

01 procedures, and then to reduce the nitro group to an amino
02 group using conventional procedures. Aromatic nitro groups
03 may be reduced to amino groups using a number of procedures
04 that are well known in the art. For example, aromatic nitro
05 groups may be reduced under catalytic hydrogenation
06 conditions; or by using a reducing metal, such as zinc, tin,
07 iron and the like, in the presence of an acid, such as
08 dilute hydrochloric acid.

09
10 Generally, reduction of the nitro group by catalytic
11 hydrogenation is preferred. Typically, this reaction is
12 conducted using about 1 to 4 atmospheres of hydrogen and a
13 platinum or palladium catalyst, such as palladium on carbon.
14 The reaction is typically carried out at a temperature of
15 about 0°C to about 100°C for about 1 to 24 hours in an inert
16 solvent, such as ethanol, ethyl acetate and the like.
17 Hydrogenation of aromatic nitro groups is discussed in
18 further detail in, for example, P. N. Rylander, *Catalytic*
19 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic
20 Press (1979); and *Organic Synthesis, Collective Vol. I*,
21 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);
22 and references cited therein.

23

24 Fuel Compositions

25

26 The polyalkyl aromatic esters of the present invention are
27 useful as additives in hydrocarbon fuels to prevent and
28 control engine deposits, particularly intake valve deposits.
29 The proper concentration of additive necessary to achieve
30 the desired deposit control varies depending upon the type
31 of fuel employed, the type of engine, and the presence of
32 other fuel additives.

33

34

-20-

01 In general, the concentration of the polyalkyl aromatic
02 esters of this invention in hydrocarbon fuel will range from
03 about 50 to about 2500 parts per million (ppm) by weight,
04 preferably from 75 to 1,000 ppm. When other deposit control
05 additives are present, a lesser amount of the present
06 additive may be used.

07
08 The polyalkyl aromatic esters of the present invention may
09 be formulated as a concentrate using an inert stable
10 oleophilic (i.e., dissolves in gasoline) organic solvent
11 boiling in the range of about 150°F to 400°F (about 65°C to
12 205°C). Preferably, an aliphatic or an aromatic hydrocarbon
13 solvent is used, such as benzene, toluene, xylene or higher-
14 boiling aromatics or aromatic thinners. Aliphatic alcohols
15 containing about 3 to 8 carbon atoms, such as isopropanol,
16 isobutylcarbinol, n-butanol and the like, in combination
17 with hydrocarbon solvents are also suitable for use with the
18 present additives. In the concentrate, the amount of the
19 additive will generally range from about 10 to about
20 70 weight percent, preferably 10 to 50 weight percent, more
21 preferably from 20 to 40 weight percent.

22
23 In gasoline fuels, other fuel additives may be employed with
24 the additives of the present invention, including, for
25 example, oxygenates, such as t-butyl methyl ether, antiknock
26 agents, such as methylcyclopentadienyl manganese
27 tricarbonyl, and other dispersants/detergents, such as
28 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
29 succinimides. Additionally, antioxidants, metal
30 deactivators and demulsifiers may be present.

31
32 In diesel fuels, other well-known additives can be employed,
33 such as pour point depressants, flow improvers, cetane
34 improvers, and the like.

-21-

01 A fuel-soluble, nonvolatile carrier fluid or oil may also be
02 used with the polyalkyl aromatic esters of this invention.
03 The carrier fluid is a chemically inert hydrocarbon-soluble
04 liquid vehicle which substantially increases the nonvolatile
05 residue (NVR), or solvent-free liquid fraction of the fuel
06 additive composition while not overwhelmingly contributing
07 to octane requirement increase. The carrier fluid may be a
08 natural or synthetic oil, such as mineral oil, refined
09 petroleum oils, synthetic polyalkanes and alkenes, including
10 hydrogenated and unhydrogenated polyalphaolefins, and
11 synthetic polyoxyalkylene-derived oils, such as those
12 described, for example, in U.S. Patent No. 4,191,537 to
13 Lewis, and polyesters, such as those described, for example,
14 in U.S. Patent Nos. 3,756,793 and 5,004,478 to Robinson and
15 Vogel et al., respectively, and in European Patent
16 Application Nos. 356,726 and 382,159, published March 7,
17 1990 and August 16, 1990, respectively.

18
19 These carrier fluids are believed to act as a carrier for
20 the fuel additives of the present invention and to assist in
21 removing and retarding deposits. The carrier fluid may also
22 exhibit synergistic deposit control properties when used in
23 combination with a polyalkyl aromatic ester of this
24 invention.

25
26 The carrier fluids are typically employed in amounts ranging
27 from about 100 to about 5000 ppm by weight of the
28 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
29 fuel. Preferably, the ratio of carrier fluid to deposit
30 control additive will range from about 0.5:1 to about 10:1,
31 more preferably from 1:1 to 4:1, most preferably about 2:1.

32
33 When employed in a fuel concentrate, carrier fluids will
34 generally be present in amounts ranging from about 20 to

-22-

01 about 60 weight percent, preferably from 30 to 50 weight
02 percent.

03

04

EXAMPLES

05

06 The following examples are presented to illustrate specific
07 embodiments of the present invention and synthetic
08 preparations thereof; and should not be interpreted as
09 limitations upon the scope of the invention.

10

11

Example 1

12

13

Preparation of Polyisobutyl-4-Nitrobenzoate

14

15 4-Nitrobenzoyl chloride (12.7 grams) was combined with
16 47.6 grams of polyisobutanol (molecular weight average 984,
17 prepared via hydroformylation of Amoco H-100 polyisobutene)
18 and 300 mL of anhydrous toluene. Triethylamine (10.0 mL)
19 and 4-dimethylaminopyridine (4.2 grams) were then added and
20 the resulting mixture heated to reflux under nitrogen for
21 sixteen hours. The reaction was cooled to room temperature
22 and diluted with diethyl ether. The organic layer was
23 washed twice with 1% aqueous hydrochloric acid, twice with
24 aqueous sodium bicarbonate solution, and once with brine.
25 The organic layer was then dried over anhydrous magnesium
26 sulfate, filtered and the solvents removed in vacuo to yield
27 41.9 grams of a yellow oil. The oil was chromatographed on
28 silica gel, eluting with hexane/ethylacetate/ethanol
29 (9:0.8:0.2) to yield 37.2 grams of the desired product as a
30 light yellow oil. IR (neat) 1725 cm^{-1} , ^1H NMR (CDCl_3) δ
31 8.3, 8.2 (AB quartet, 4H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).

32

33

34

-23-

Example 2Preparation of Polyisobutyl-4-Aminobenzoate

A solution of 30.75 grams of the product from Example 1 in 220 mL of ethyl acetate containing 3.5 grams of 10% palladium on charcoal was hydrogenated at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yielded 29.44 grams of the desired product as a light yellow oil. IR (neat) 1709, 1696 cm^{-1} . ^1H NMR (CDCl_3) δ 7.9 (d, 2H), 6.65 (d, 2H), 4.3 (t, 2H), 4.1 (bs, 2H), 0.6-1.8 (m, 137H).

Example 3Preparation of Polyisobutyl-3-Nitro-4-Hydroxybenzoate

To a flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 35.0 grams of polyisobutanol (molecular weight average 984, prepared via hydroformylation of Amoco H-100 polyisobutene), 11.0 grams of 3-nitro-4-hydroxybenzoic acid and 0.86 grams of p-toluene sulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 500 mL of diethyl ether. The organic phase was washed twice with saturated aqueous sodium bicarbonate solution, once with brine, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 35.0 grams of a brown oil. The oil was chromatographed on silica gel eluting with hexane/ethyl acetate/ethanol (8:1.8:0.2) to yield 25.4 grams of the desired product as a light brown oil. IR (neat) 1721 cm^{-1} .

-24-

01 ¹H NMR (CDCl₃) δ 10.9 (s, 1H), 8.85 (s, 1H), 8.25 (d, 1H),
02 7.2 (d, 1H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).
03

04 Example 4
05

06 Preparation of Polyisobutyl-3-Hydroxy-4-Nitrobenzoate
07

08 To a flask equipped with a mechanical stirrer, thermometer,
09 Dean-Stark trap, reflux condensor and nitrogen inlet was
10 added 35.0 grams of polyisobutanol (molecular weight average
11 984, prepared via hydroformylation of Amoco H-100
12 polyisobutene), 11.0 grams of 3-hydroxy-4-nitrobenzoic acid
13 and 0.86 grams of p-toluene sulfonic acid. The mixture was
14 stirred at 130°C for sixteen hours, cooled to room
15 temperature and diluted with 500 mL of diethyl ether. The
16 organic phase was washed twice with saturated aqueous sodium
17 bicarbonate solution, once with brine, dried over anhydrous
18 magnesium sulfate, filtered and concentrated in vacuo to
19 yield 37.8 grams of a black oil. The oil was
20 chromatographed on silica gel eluting with hexane/ethyl
21 acetate/ethanol (8:1.8:0.2) to yield 27.9 grams of the
22 desired product as a brown oil. IR (neat) 1731cm⁻¹. ¹H NMR
23 (CDCl₃) δ 10.5 (s, 1H), 8.2 (d, 1H), 7.8 (s, 1H), 7.65 (d,
24 1H), 4.35 (t, 2H), 0.6-1.8 (m, 137H).
25

26 Example 5
27

28 Preparation of Polyisobutyl-3-Amino-4-Hydroxybenzoate
29

30 A solution of 19.0 grams of the product from Example 3 in
31 200 mL of ethyl acetate containing 3.0 grams of 10%
32 palladium on charcoal was hydrogenolyzed at 35-40 psi for
33 sixteen hours on a Parr low-pressure hydrogenator. Catalyst
34

-25-

01 filtration and removal of the solvent in vacuo yielded
02 17.4 grams of the desired product as a light brown oil. IR
03 (neat) 1716, 1682 cm^{-1} . ^1H NMR (CDCl_3) δ 7.45 (m, 2H), 6.75
04 (d, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).
05

06 Example 6
07

08 Preparation of Polyisobutyl-3-Hydroxy-4-Aminobenzoate
09

10 A solution of 21.35 grams of the product from Example 4 in
11 200 mL of ethyl acetate containing 3.0 grams of 10%
12 palladium on charcoal was hydrogenolyzed at 35-40 psi for
13 sixteen hours on a Parr low-pressure hydrogenator. Catalyst
14 filtration and removal of the solvent in vacuo yielded
15 20.6 grams of the desired product as a light brown oil. IR
16 (neat) 1709, 1682 cm^{-1} . ^1H NMR (CDCl_3) δ 7.6 (s, 1H), 7.5
17 (d, 1H), 6.7 (d, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).
18

19 Example 7
20

21 Single-Cylinder Engine Test
22

23 The test compounds were blended in gasoline and their
24 deposit reducing capacity determined in an ASTM/CFR
25 single-cylinder engine test.
26

27 A Waukesha CFR single-cylinder engine was used. Each run
28 was carried out for 15 hours, at the end of which time the
29 intake valve was removed, washed with hexane and weighed.
30 The previously determined weight of the clean valve was
31 subtracted from the weight of the valve at the end of the
32 run. The differences between the two weights is the weight
33 of the deposit. A lesser amount of deposit indicates a
34

-26-

01 superior additive. The operating conditions of the test
02 were as follows: water jacket temperature 200°F; vacuum of
03 12 in Hg, air-fuel ratio of 12, ignition spark timing of
04 40° BTC; engine speed is 1800 rpm; the crankcase oil is a
05 commercial 30W oil.

06
07 The amount of carbonaceous deposit in milligrams on the
08 intake valves is reported for each of the test compounds in
09 Table I.

TABLE I

Intake Valve Deposit Weight
(in milligrams)

14 Sample ¹	Run 1	Run 2	Average
15 Base Fuel	176.4	179.2	177.8
16 Example 1	171.0	159.4	165.2
17 Example 2	10.0	16.6	13.3
18 Example 3	130.0	143.5	136.8
19 Example 4	139.0	127.0	133.0
20 Example 5	0.0	0.4	0.2
21 Example 6	0.0	0.2	0.1

22
23
24 ¹At 200 parts per million actives (ppma).

25
26 The base fuel employed in the above single-cylinder engine
27 tests was a regular octane unleaded gasoline containing no
28 fuel detergent. The test compounds were admixed with the
29 base fuel to give a concentration of 200 ppma (parts per
30 million actives).

31
32 The data in Table I illustrates the significant reduction in
33 intake valve deposits provided by the polyalkyl aromatic
34

-27-

01 esters of the present invention (Examples 1, 2, 3, 4, 5 and
02 6) compared to the base fuel.

03

04 Example 8

05

06 Multicylinder Engine Test

07

08 The polyalkyl aromatic esters of the present invention were
09 tested in a laboratory multicylinder engine to evaluate
10 their intake valve and combustion chamber deposit control
11 performance. The test engine was a 4.3 liter, TBI (throttle
12 body injected), V6 engine manufactured by General Motors
13 Corporation.

14

15 The major engine dimensions are set forth in Table II:

16

17

18 Table II

19

20 Engine Dimensions

21

21	Bore	10.16 cm
22	Stroke	8.84 cm
23	Displacement Volume	4.3 liter
24	Compression Ratio	9.3:1

25

26

27 The test engine was operated for 40 hours (24 hours a day)
28 on a prescribed load and speed schedule representative of
29 typical driving conditions. The cycle for engine operation
30 during the test is set forth in Table III.

31

32

33

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-28-

Table III

Engine Driving Cycle

Step	Mode	Time in Mode [Sec] ¹	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

¹ All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

-29-

Table IV
Multicylinder Engine Test Results

Sample ¹		Intake Valve Deposits ²	Combustion Chamber Deposits ²
Base Fuel	Run 1	710	2339
	Run 2	962	2059
	Average	836	2199
Example 5	Run 1	165	2596
	Run 2	143	2566
	Average	154	2581

¹ At 200 parts per million actives (ppma) plus 800 ppm Chevron 500 neutral oil.

² In milligrams (mg).

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives) plus 800 ppm of the carrier fluid Chevron 500 neutral oil.

The data in Table IV illustrates the significant reduction in intake valve deposits provided by the polyalkyl aromatic esters of the present invention (Example 5) compared to the base fuel. Moreover, the data in Table IV further demonstrates that the polyalkyl aromatic esters of the present invention do not contribute significantly to combustion chamber deposits.

-30-

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05

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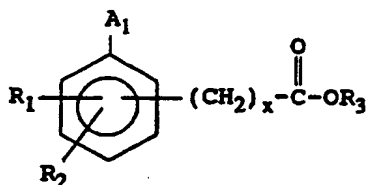
30

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32

33

34



wherein A_1 is nitro, amino, *N*-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or *N,N*-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

R_1 and R_2 are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R_3 is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10.

2. The compound according to Claim 1, wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms.

3. The compound according to Claim 2, wherein R_1 is hydrogen or hydroxy.

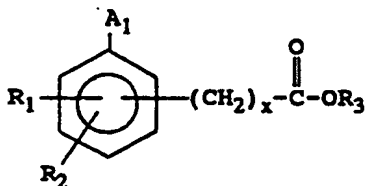
4. The compound according to Claim 3, wherein R_1 is hydroxy.

-31-

- 01 5. The compound according to Claim 1, wherein R_2 is
02 hydrogen.
03
- 04 6. The compound according to Claim 1, wherein x is 0, 1 or
05 2.
06
- 07 7. The compound according to Claim 6, wherein R_1 and R_2
08 are hydrogen, and x is 0.
09
- 10 8. The compound according to Claim 6, wherein R_1 is
11 hydroxy, R_2 is hydrogen, and x is 0.
12
- 13 9. The compound according to Claim 17, wherein A_1 is nitro
14 or amino.
15
- 16 10. The compound according to Claim 9, wherein A_1 is amino.
17
- 18 11. The compound according to Claim 1, wherein R_3 is a
19 polyalkyl group having a weight average molecular
20 weight in the range of about 500 to 5,000.
21
- 22 12. The compound according to Claim 11, wherein R_3 has a
23 weight average molecular weight in the range of about
24 500 to 3,000.
25
- 26 13. The compound according to Claim 12, wherein R_3 has a
27 weight average molecular weight in the range of about
28 600 to 2,000.
29
- 30 14. The compound according to Claim 1, wherein R_3 is a
31 polyalkyl group derived from polypropylene, polybutene,
32 or polyalphaolefin oligomers of 1-octene or 1-decene.
33
34

-32-

- 01 15. The compound according to Claim 14, wherein R_3 is
 02 derived from polyisobutene.
 03
- 04 16. The compound according to Claim 15, wherein the
 05 polyisobutene contains at least about 20% of a
 06 methylvinylidene isomer.
 07
- 08 17. A fuel composition comprising a major amount of
 09 hydrocarbons boiling in the gasoline or diesel range
 10 and an effective detergent amount of a compound of the
 11 formula:
 12



19 wherein A_1 is nitro, amino, *N*-alkylamino wherein the
 20 alkyl group contains 1 to 6 carbon atoms, or
 21 *N,N*-dialkylamino wherein each alkyl group independently
 22 contains 1 to 6 carbon atoms;
 23

24 R_1 and R_2 are independently hydrogen, hydroxy, lower
 25 alkyl having 1 to 6 carbon atoms, or lower alkoxy
 26 having 1 to 6 carbon atoms;
 27

28 R_3 is a polyalkyl group having a weight average
 29 molecular weight in the range of about 450 to 5,000;
 30 and x is an integer from 0 to 10.
 31
 32
 33
 34

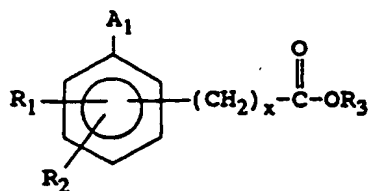
-33-

- 01 18. The fuel composition according to Claim 17, wherein R_1
02 is hydrogen, hydroxy, or lower alkyl having 1 to 4
03 carbon atoms.
04
- 05 19. The fuel composition according to Claim 18, wherein R_1
06 is hydrogen or hydroxy.
07
- 08 20. The fuel composition according to Claim 19, wherein R_1
09 is hydroxy.
10
- 11 21. The fuel composition according to Claim 1, wherein R_2
12 is hydrogen.
13
- 14 22. The fuel composition according to Claim 17, wherein x
15 is 0, 1 or 2.
16
- 17 23. The fuel composition according to Claim 22, wherein R_1
18 and R_2 are hydrogen, and x is 0.
19
- 20 24. The fuel composition according to Claim 22, wherein R_1
21 is hydroxy, R_2 is hydrogen, and x is 0.
22
- 23 25. The fuel composition according to Claim 17, wherein A_1
24 is nitro or amino.
25
- 26 26. The fuel composition according to Claim 25, wherein A_1
27 is amino.
28
- 29 27. The fuel composition according to Claim 17, wherein R_3
30 is a polyalkyl group having a weight average molecular
31 weight in the range of about 500 to 5,000.
32
33
34

-34-

- 01 28. The fuel composition according to Claim 27, wherein R_3
02 has a weight average molecular weight in the range of
03 about 500 to 3,000.
04
- 05 29. The fuel composition according to Claim 28, wherein R_3
06 has a weight average molecular weight in the range of
07 about 600 to 2,000.
08
- 09 30. The fuel composition according to Claim 17, wherein R_3
10 is a polyalkyl group derived from polypropylene,
11 polybutene, or polyalphaolefin oligomers of 1-octene or
12 1-decene.
13
- 14 31. The fuel composition according to Claim 30, wherein R_3
15 is derived from polyisobutene.
16
- 17 32. The fuel composition according to Claim 31, wherein the
18 polyisobutene contains at least about 20% of a
19 methylvinylidene isomer.
20
- 21 33. The fuel composition according to Claim 17, wherein
22 said composition contains about 50 to about 2500 parts
23 per million by weight of said compound.
24
- 25 34. A fuel concentrate comprising an inert stable
26 oleophilic organic solvent boiling in the range of from
27 about 150°F to 400°F and from about 10 to about 70
28 weight percent of a compound of the formula:
29
30
31
32
33
34

-35-



wherein A_1 is nitro, amino, *N*-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or *N,N*-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

R_1 and R_2 are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R_3 is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10.

35. The fuel concentrate according to Claim 34, wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms.

36. The fuel concentrate according to Claim 35, wherein R_1 is hydrogen or hydroxy.

37. The fuel concentrate according to Claim 36, wherein R_1 is hydroxy.

38. The fuel concentrate according to Claim 34, wherein R_2 is hydrogen.

-36-

- 01 39. The fuel concentrate according to Claim 34, wherein x
02 is 0, 1 or 2.
03
- 04 40. The fuel concentrate according to Claim 39, wherein R₁
05 and R₂ are hydrogen, and x is 0.
06
- 07 41. The fuel concentrate according to Claim 39, wherein R₁
08 is hydroxy, R₂ is hydrogen, and x is 0.
09
- 10 42. The fuel concentrate according to Claim 34, wherein A₁
11 is nitro or amino.
12
- 13 43. The fuel concentrate according to Claim 42, wherein A₁
14 is amino.
15
- 16 44. The fuel concentrate according to Claim 34, wherein R₃
17 is a polyalkyl group having a weight average molecular
18 weight in the range of about 500 to 5,000.
19
- 20 45. The fuel concentrate according to Claim 44, wherein R₃
21 has a weight average molecular weight in the range of
22 about 500 to 3,000.
23
- 24 46. The fuel concentrate according to Claim 45, wherein R₃
25 has a weight average molecular weight in the range of
26 about 600 to 2,000.
27
- 28 47. The fuel concentrate according to Claim 34, wherein R₃
29 is a polyalkyl group derived from polypropylene,
30 polybutene, or polyalphaolefin oligomers of 1-octene or
31 1-decene.
32
33
34

-37-

- 01 48. The fuel concentrate according to Claim 47, wherein R_3
02 is derived from polyisobutene.
03
- 04 49. The fuel concentrate according to Claim 48, wherein the
05 polyisobutene contains at least about 20% of a
06 methylvinylidene isomer.
07
08
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/13797

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18; C07C 205/00, 229/00

US CL : 44/399, 410; 560/23, 43

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/399, 410; 560/23, 43

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

search terms: amino-hexyldecyl benzoic acid, nitrobenzoate, hydroxybenzoate, fuel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,252,089 (Miller) 12 August 1941, col. 1, lines 1-4, 51-55; col. 2, lines 1-29.	1-49
A	US, A, 3,929,864 (Papenfuss) 30 December 1975, see entire document.	1-16
A	US, A, 4,058,550 (Shepherd et al) 15 November 1977, see entire document.	1-16
A	JP, A, 56-169650 (Nippon) 26 December 1981, see abstract.	1-16
A	JP, A, 62-016450 (Nisshin) 24 January 1987, see abstract.	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:		T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A	document defining the general state of the art which is not considered to be of particular relevance		
E	earlier document published on or after the international filing date	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means		
P	document published prior to the international filing date but later than the priority date claimed	A	document member of the same patent family

Date of the actual completion of the international search

17 JANUARY 1995

Date of mailing of the international search report

08 MAR 1995

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